

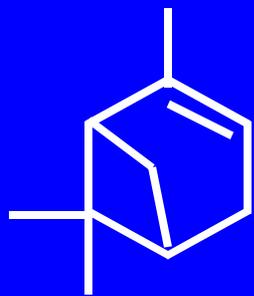
**Monoterpene and
Sesquiterpene Emissions
from Ponderosa Pine:
Implications for Secondary
Organic Aerosol Formation**

**Anita Lee, Gunnar Schade, Allen Goldstein
UC Berkeley**

GCEP Workshop: August 19, 2002

What are Monoterpenes?

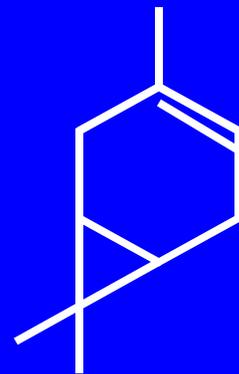
- $C_{10}H_{16}$: class of volatile organic compound
- Emitted by all conifers and some flowering plants
- Used for defense
- Many different species emitted



α -pinene



β -pinene



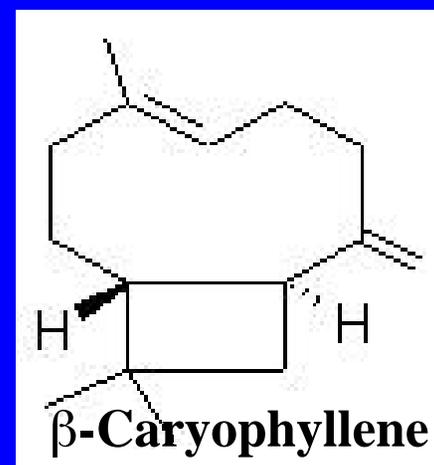
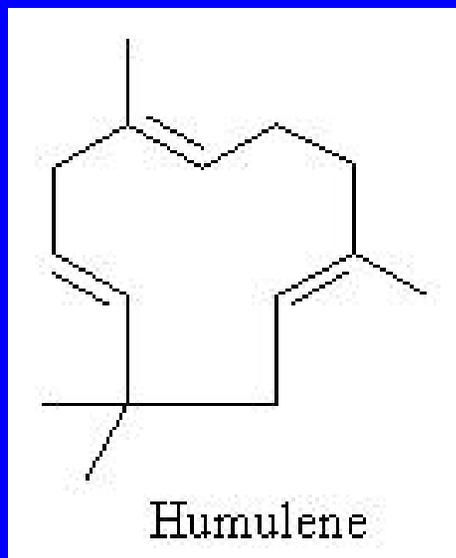
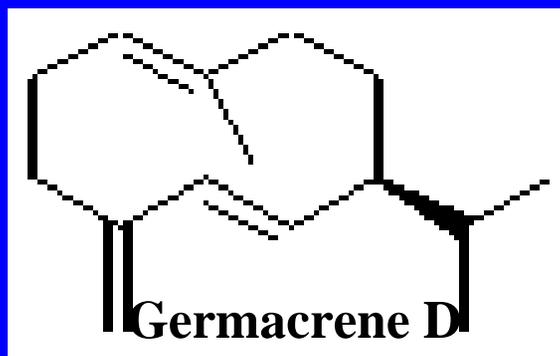
Δ -3-carene

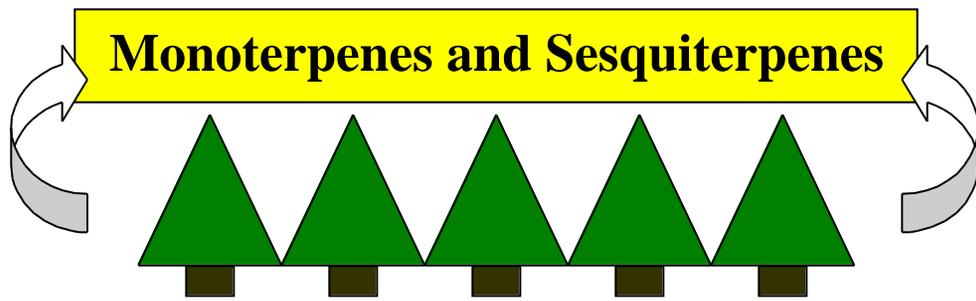
Why Monoterpenes?

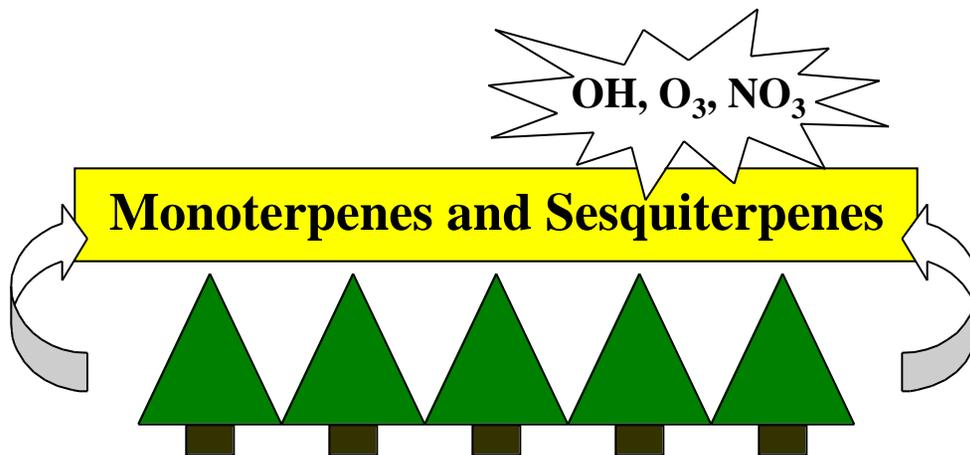
- Biogenic VOC emissions 10× greater than anthropogenic emissions
- Reactive!
- Consumes OH radical: Oxidizing capacity of the atmosphere
- Tropospheric ozone production
- Secondary organic aerosol (SOA) production

Why Sesquiterpenes?

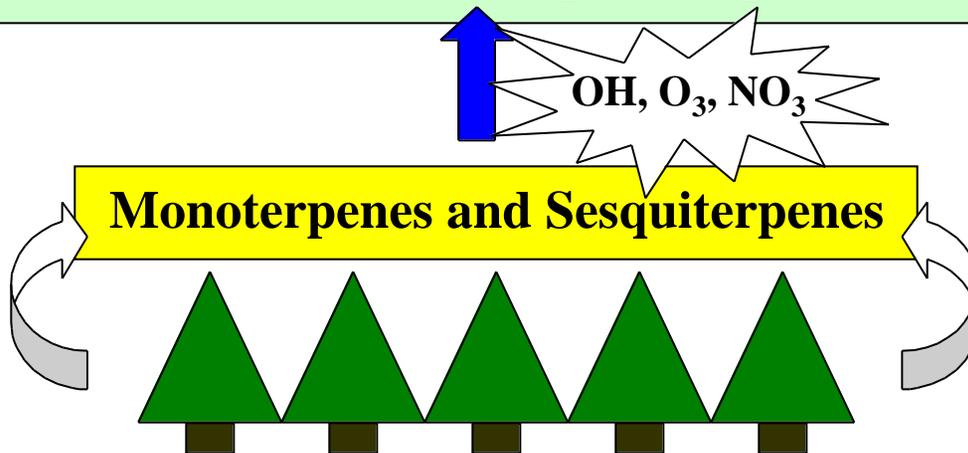
- $C_{15}H_{24}$ Heavy VOC particle phase
- More double bonds more reactive
- Currently little is known

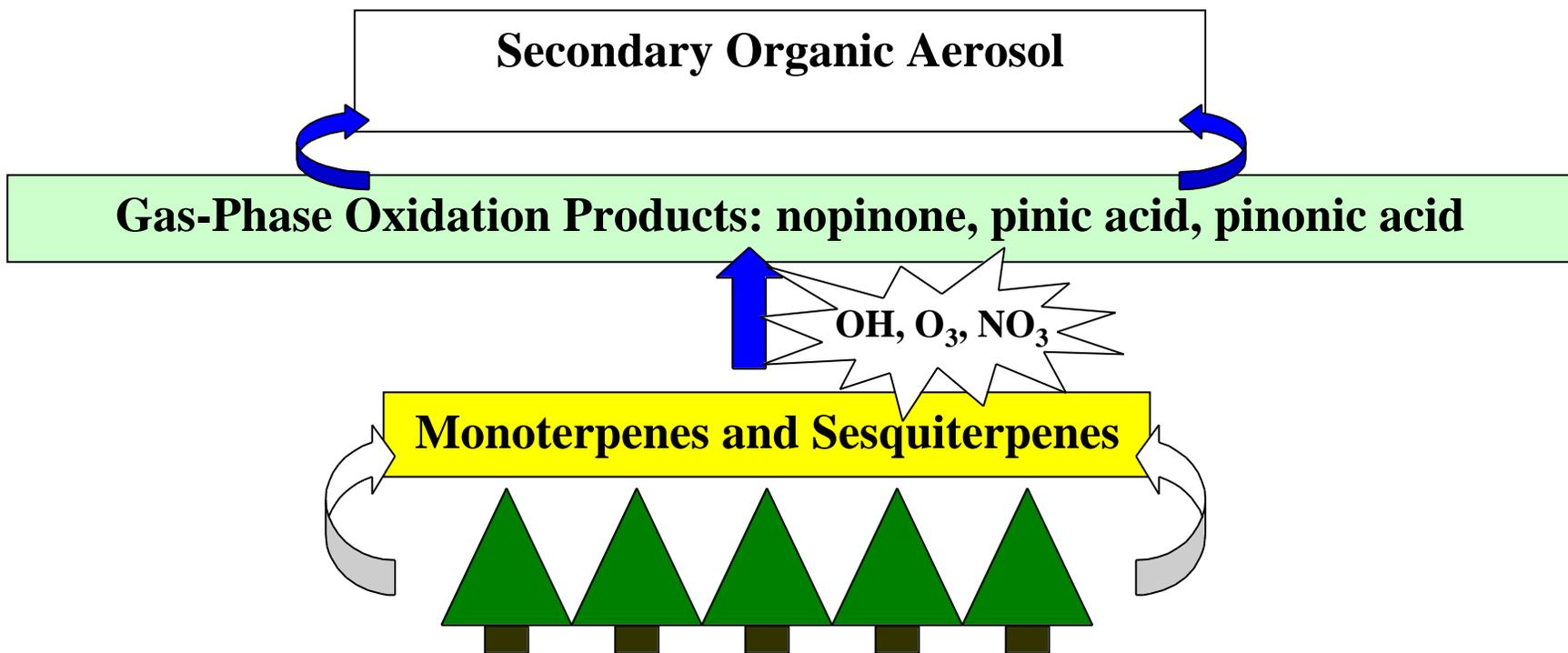


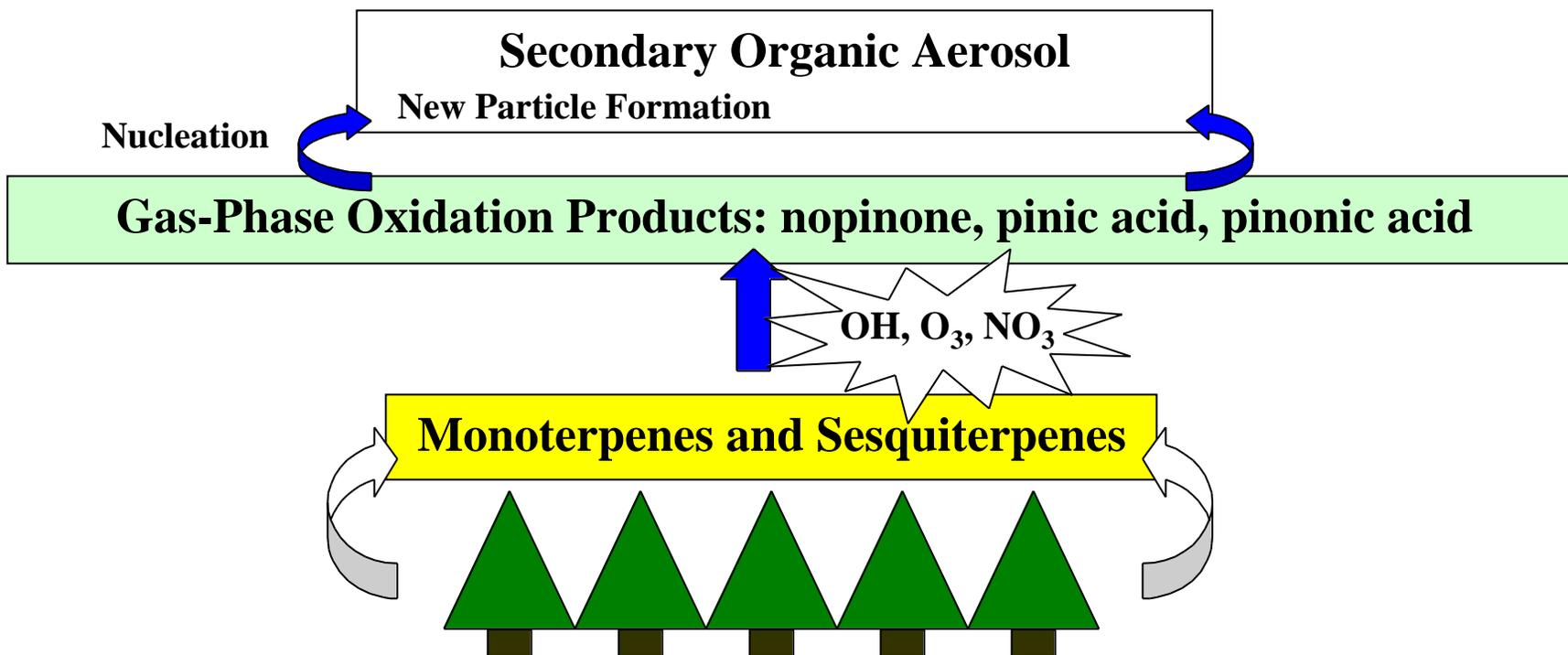


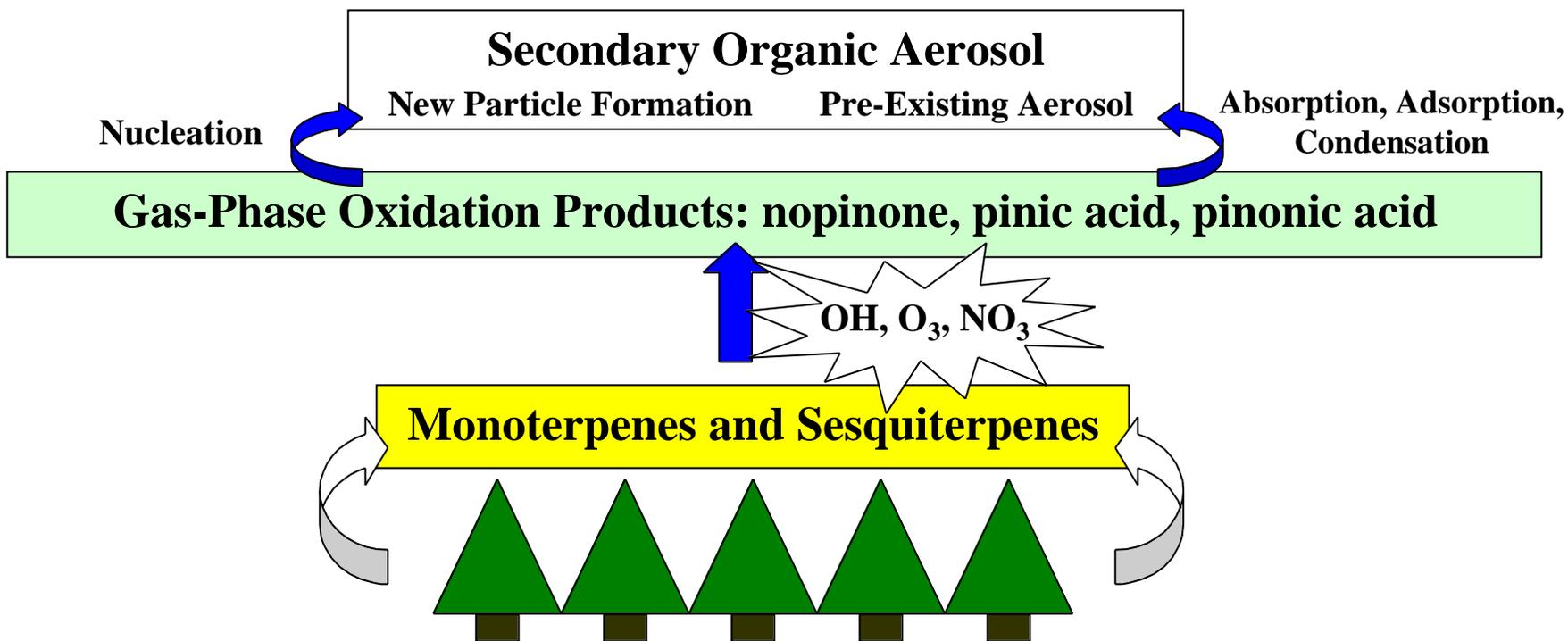


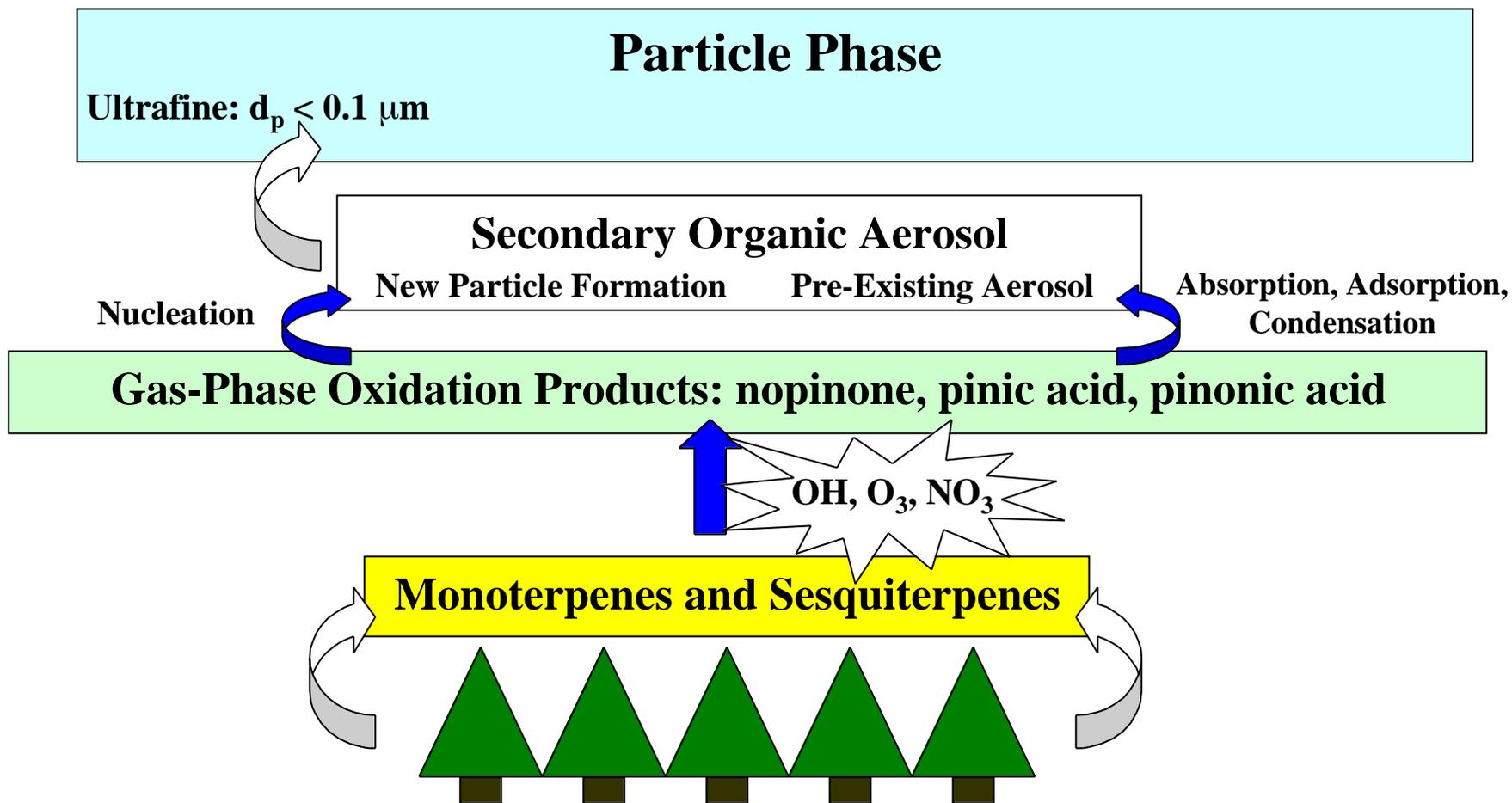
Gas-Phase Oxidation Products: nopinone, pinic acid, pinonic acid

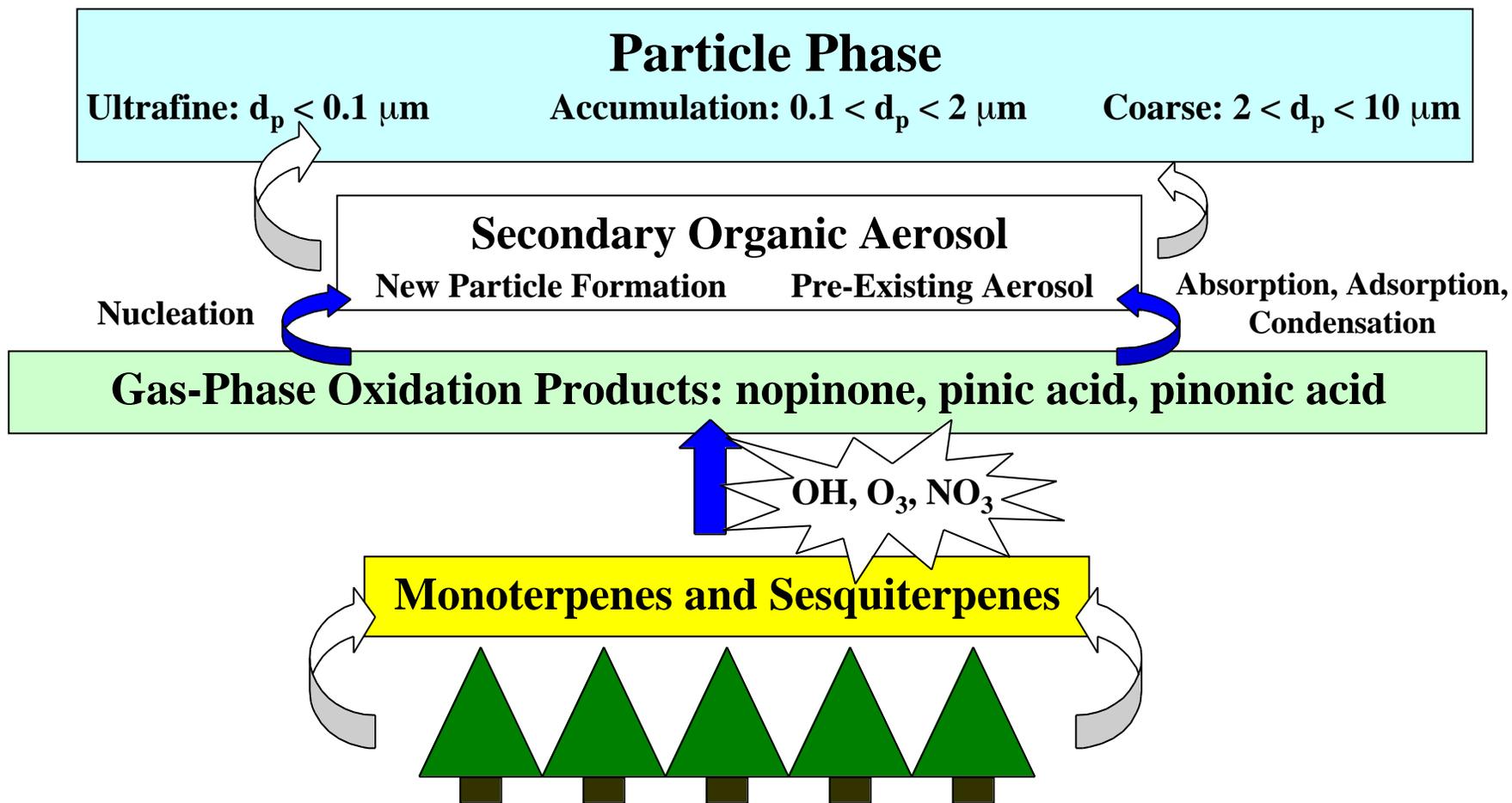


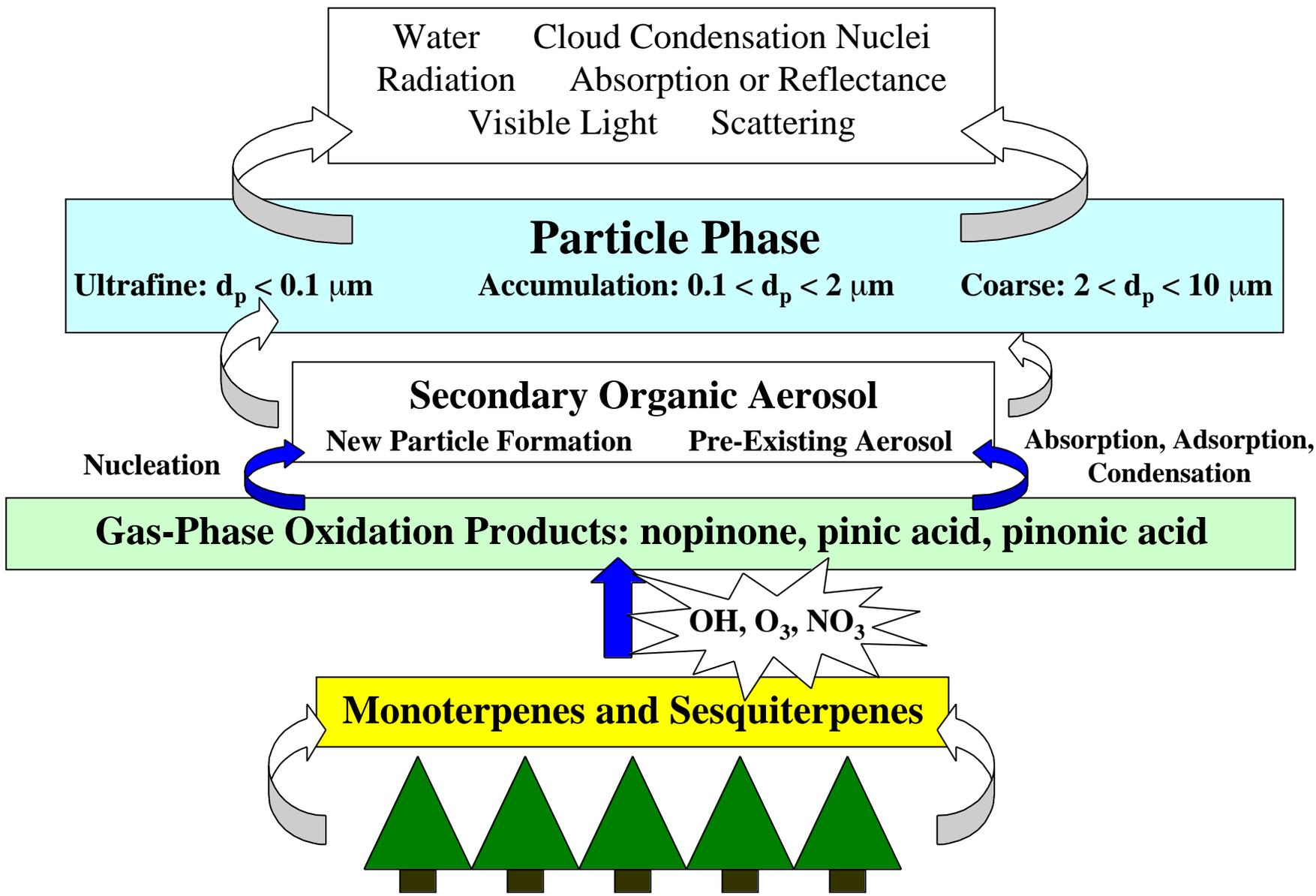












Regional and Global Effects on Climate

Water Cloud Condensation Nuclei
Radiation Absorption or Reflectance
Visible Light Scattering

Particle Phase

Ultrafine: $d_p < 0.1 \mu\text{m}$

Accumulation: $0.1 < d_p < 2 \mu\text{m}$

Coarse: $2 < d_p < 10 \mu\text{m}$

Secondary Organic Aerosol

Nucleation

New Particle Formation

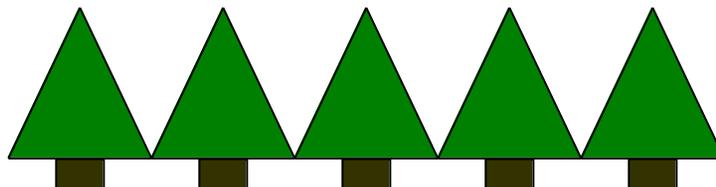
Pre-Existing Aerosol

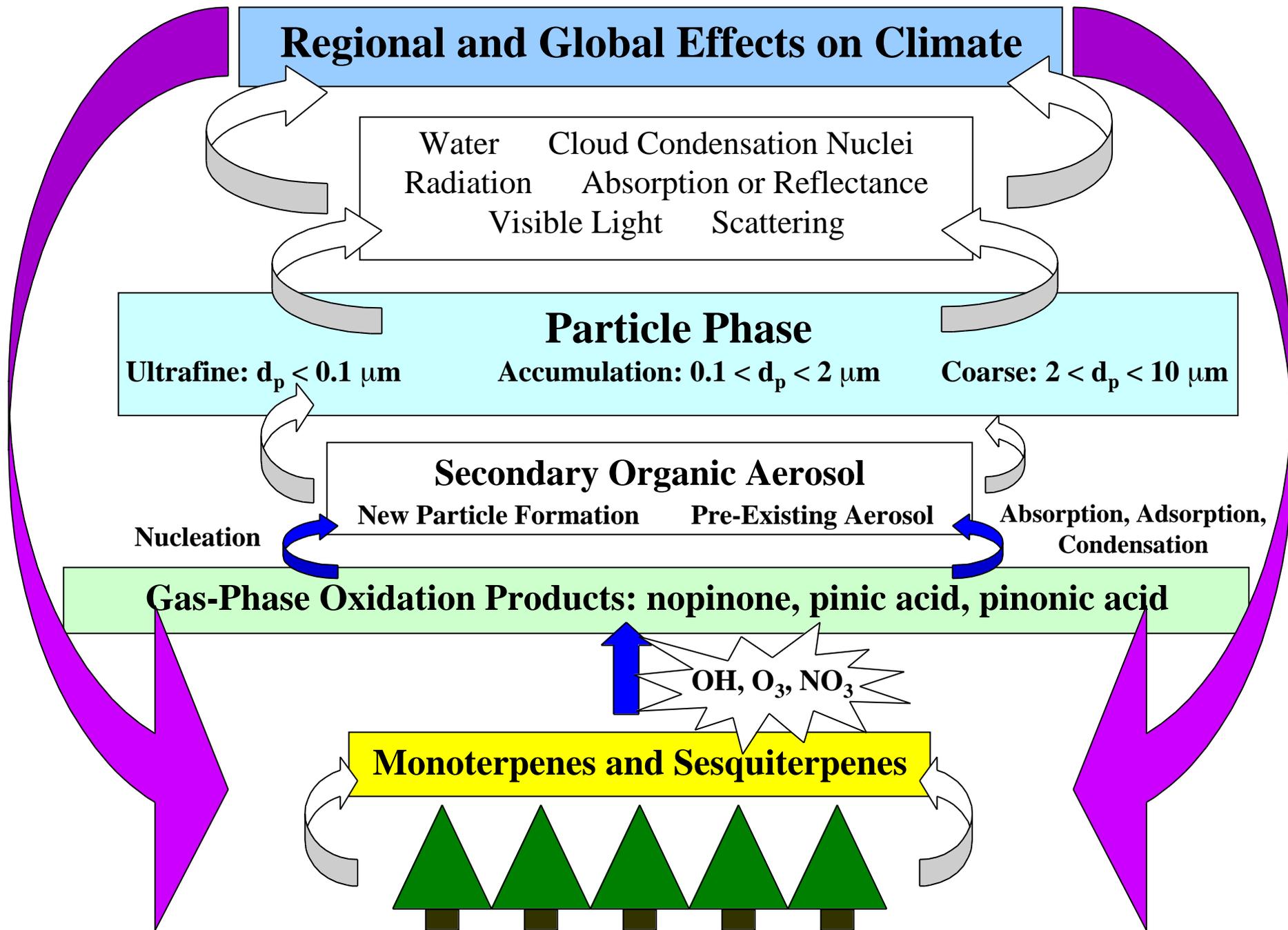
Absorption, Adsorption,
Condensation

Gas-Phase Oxidation Products: nopinone, pinic acid, pinonic acid

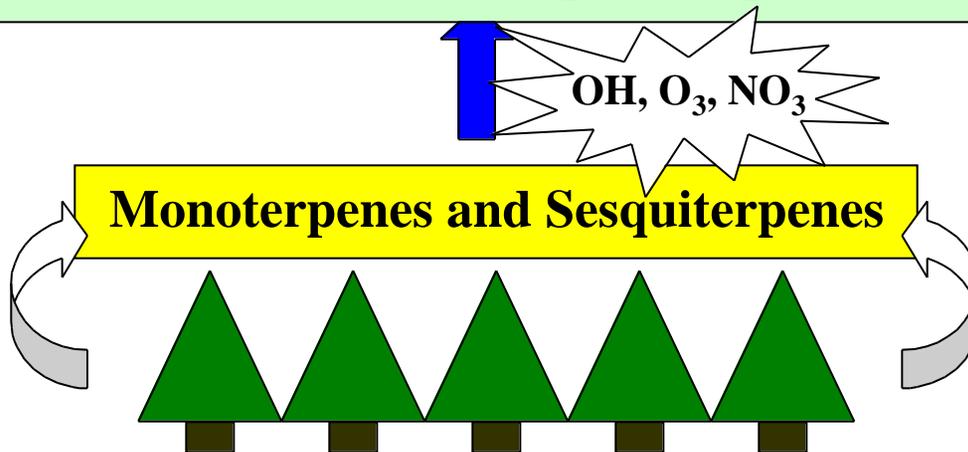
OH, O₃, NO₃

Monoterpenes and Sesquiterpenes





Gas-Phase Oxidation Products: nopinone, pinic acid, pinonic acid



Outline

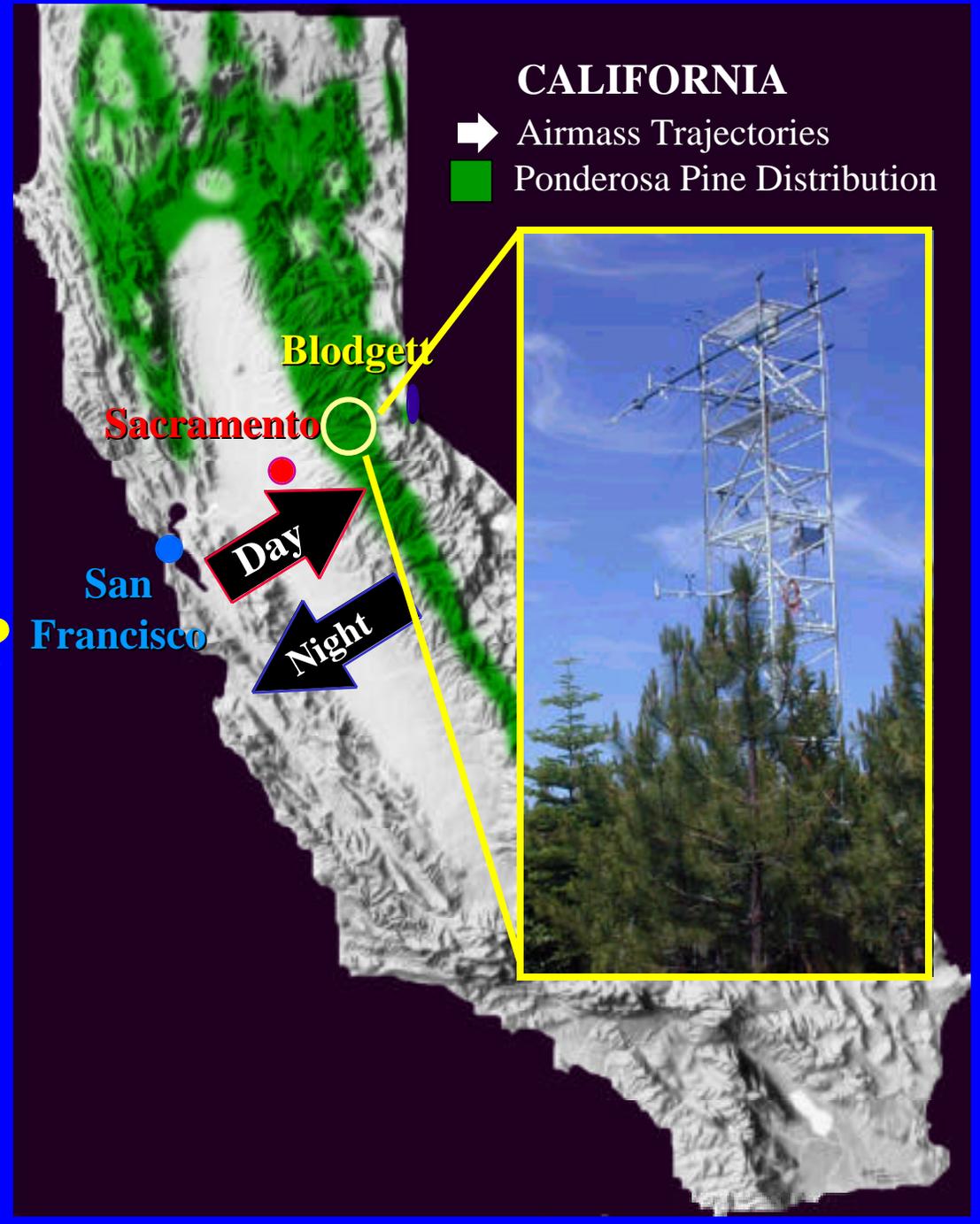
- On-going field measurements of speciated monoterpenes using GC-FID
- Laboratory chamber measurements of monoterpenes and sesquiterpenes from Ponderosa Pine
- New field measurements of total monoterpenes using PTR-MS
- Preliminary Data!

Blodgett Forest

- CO₂, H₂O, Ozone, VOC, CO and H₂ (Goldstein)
- NO_x, NO_y (Cohen)
- Aerosols (Lunden)

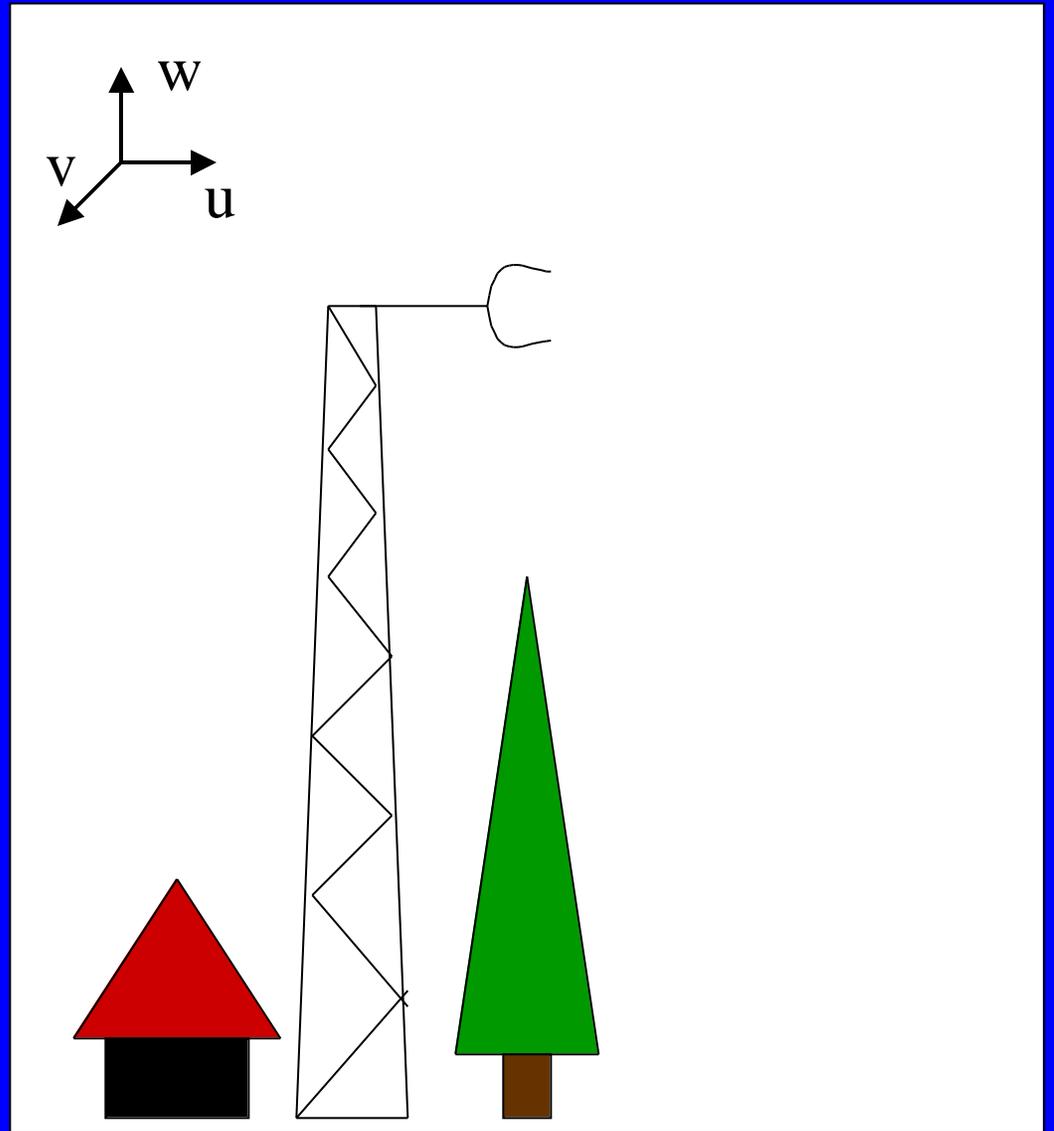
Why ponderosa pine?

- Important tree in Western U.S
- Major emitter of terpenes, MBO
- Ozone sensitive



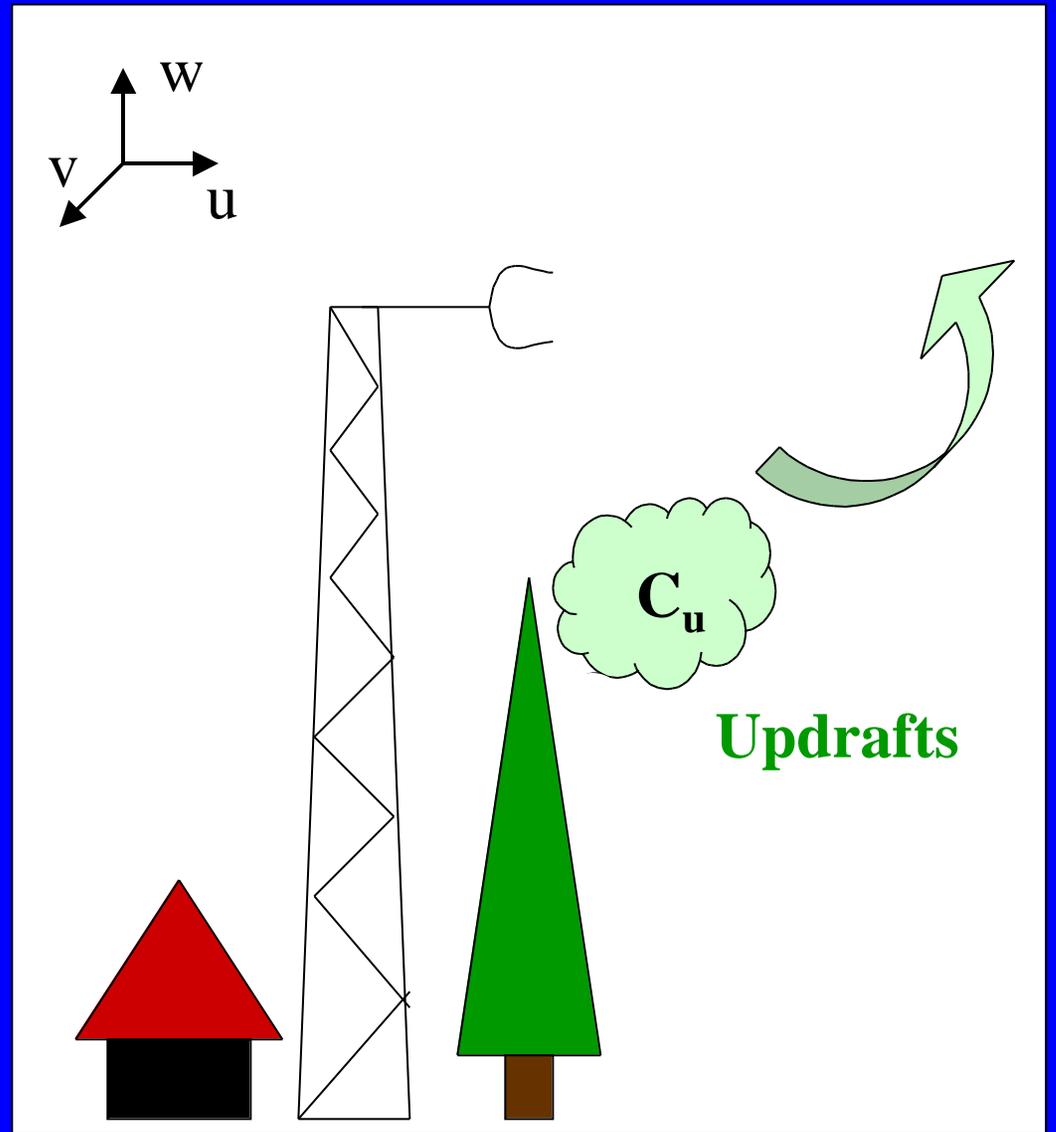
Speciated Terpene Flux

- 2 channel GC-FID
- Relaxed Eddy Accumulation



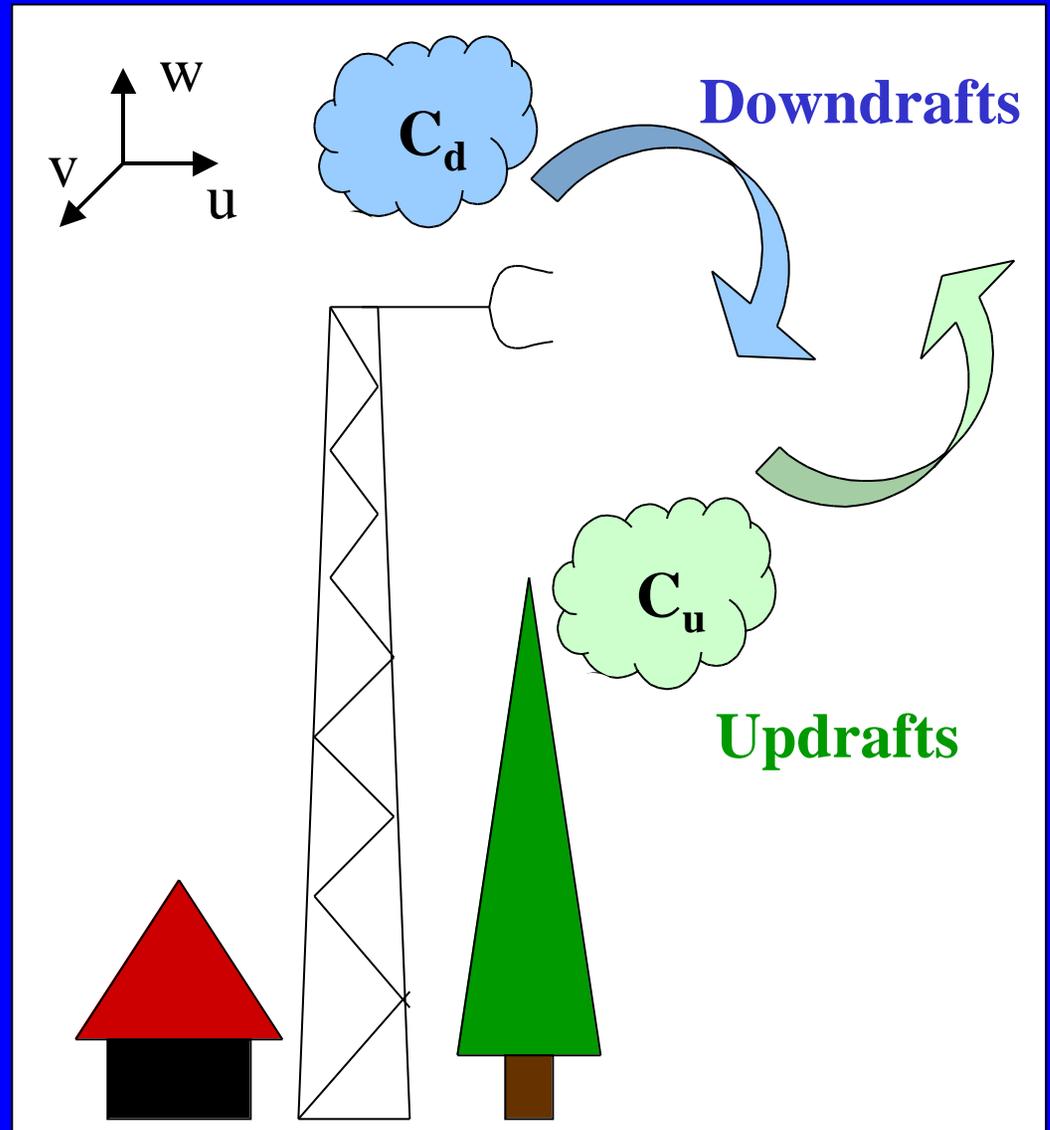
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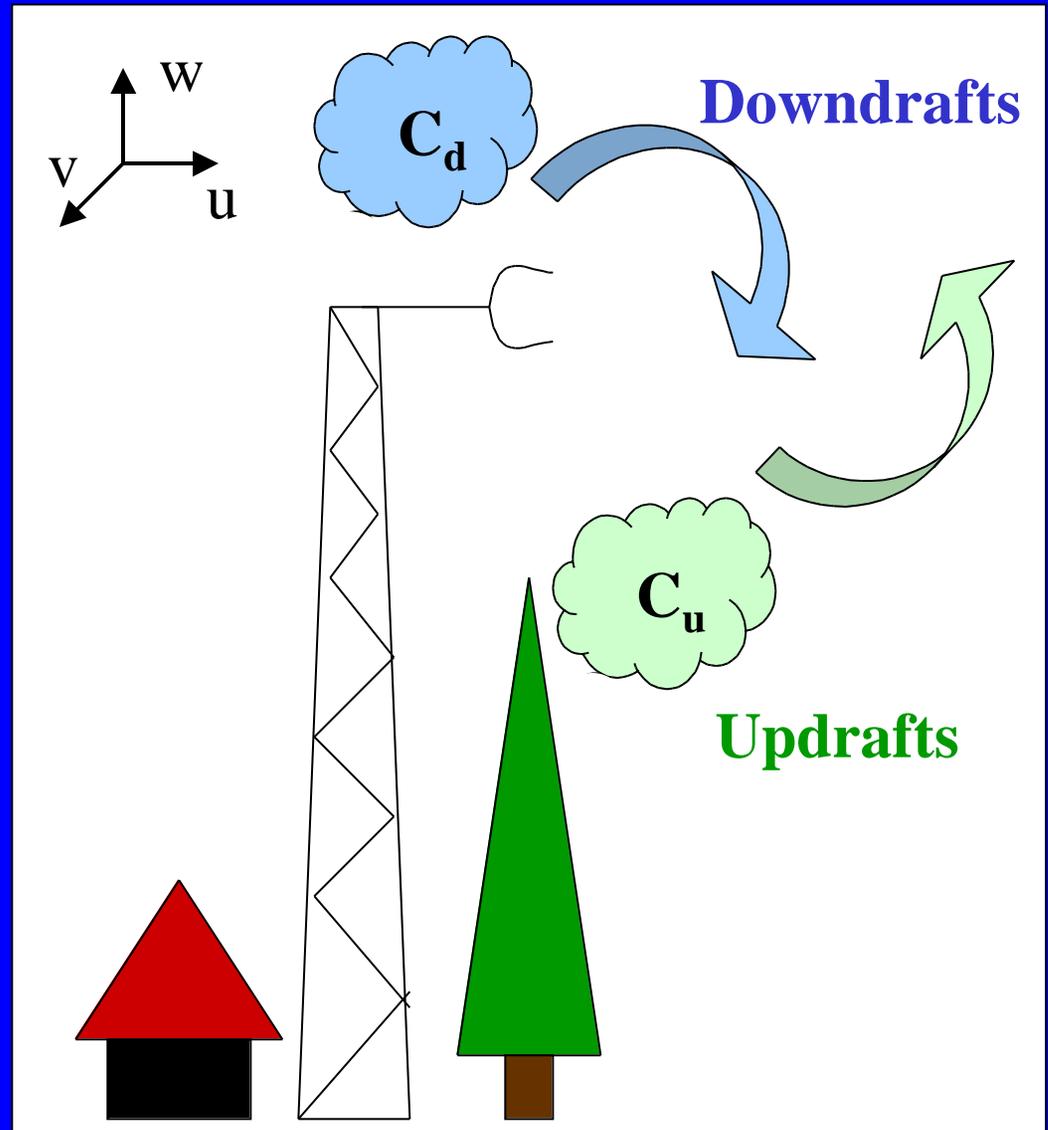
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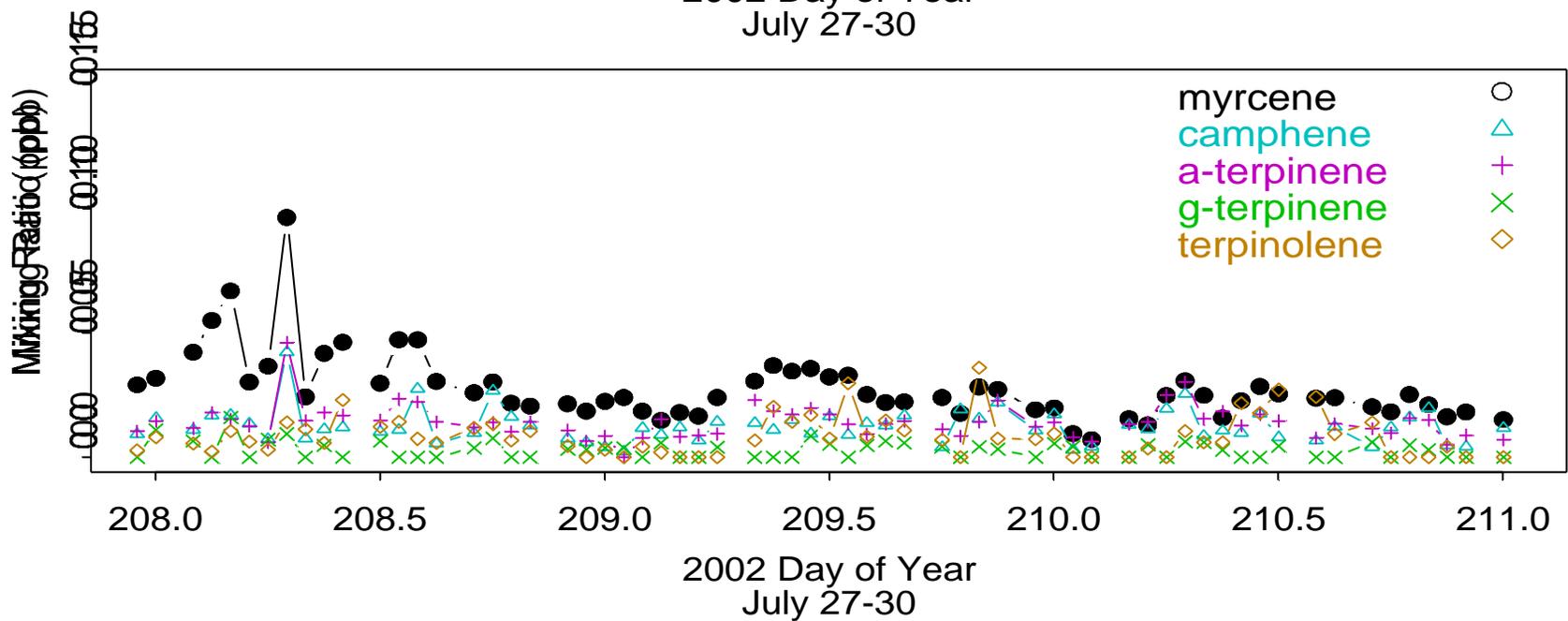
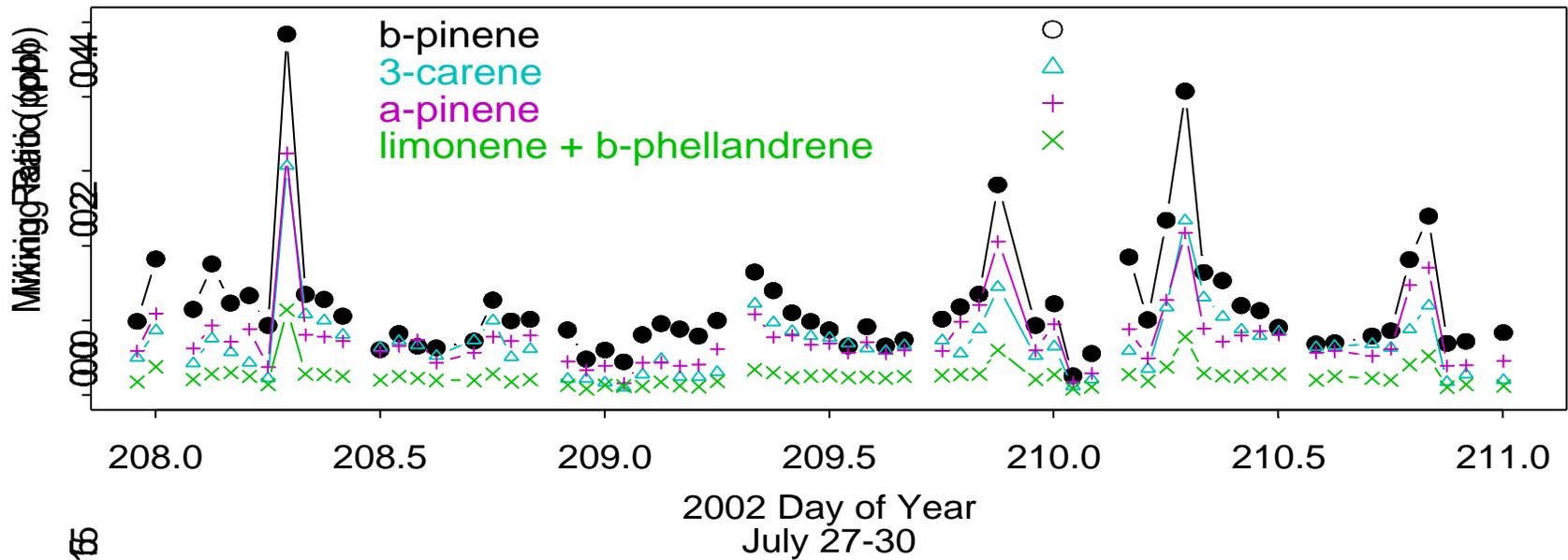


Speciated Terpene Flux

- 2 channel GC-FID
- Relaxed Eddy Accumulation
- One measurement each hour
- $F = b_w (C_{up} - C_{down})$



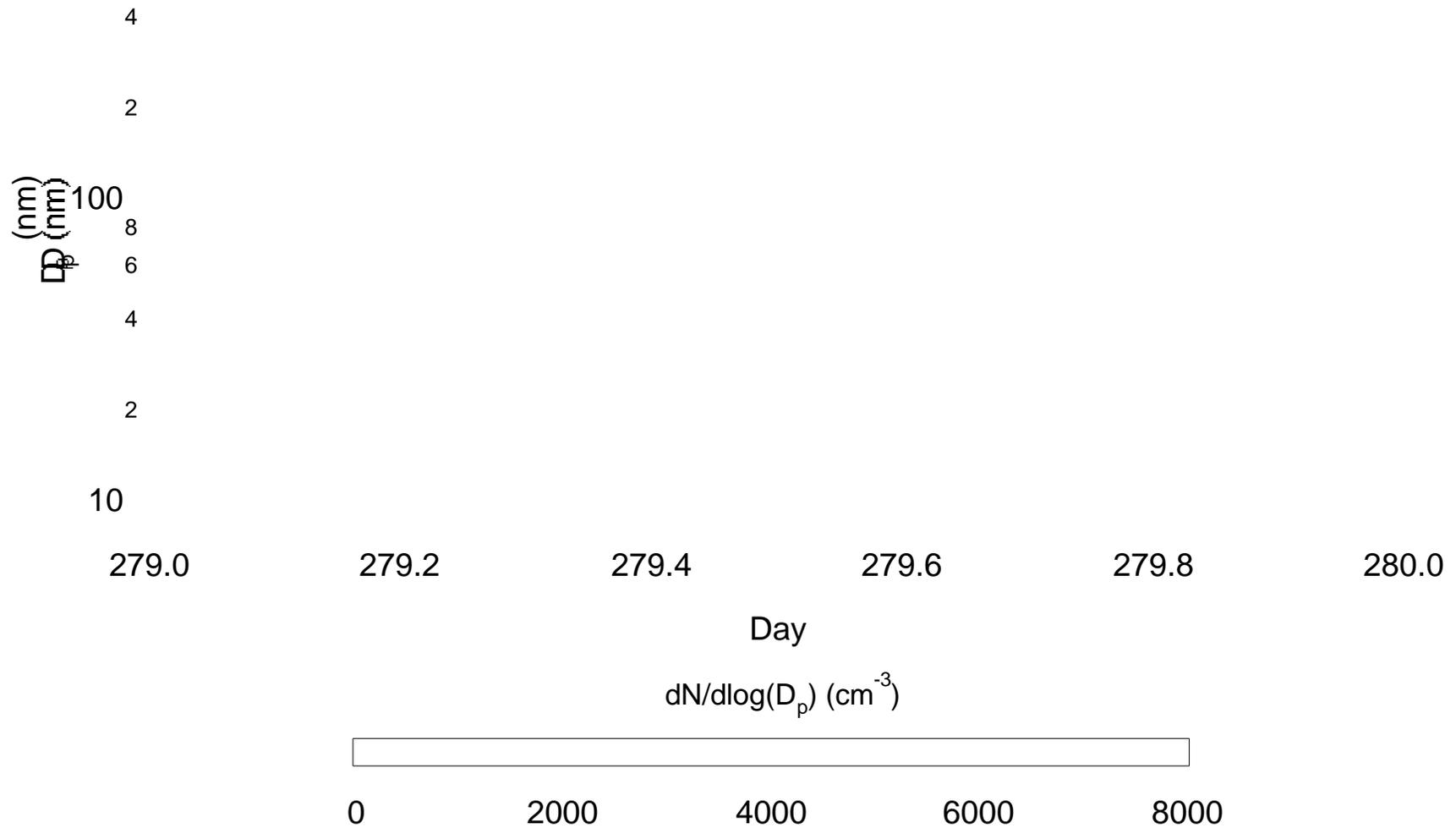
Speciated Monoterpene Mixing Ratios



New Directions

- Further understand impact of terpenes on regional air chemistry
- Link terpene oxidation with SOA production
- SOA production: 18.5 (30 - 270) Tg C year⁻¹
- Constrain SOA production from mono- and sesquiterpenes
- Explain observed nucleation events

Nucleation Burst on 10/6/01

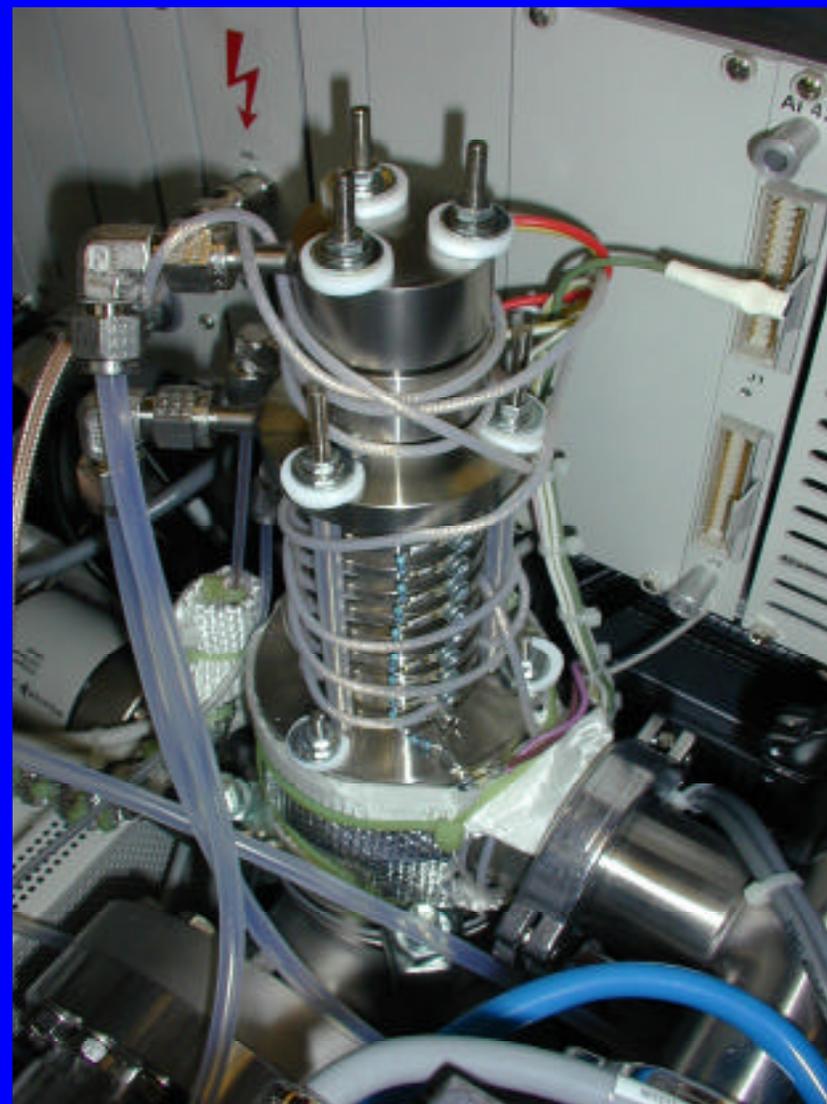


M. Lunden and D. Black, LBNL 2001

New Instrumentation

- Fast real-time measurements of terpenes and their oxidation products
- Proton Transfer Reaction Mass Spectrometer
- Quadrupole Mass Spectrometer
- Chemical ionization using H_3O^+
- Compounds with proton affinity higher than water trace atmospheric constituents
- Softer ionization Less Fragmentation

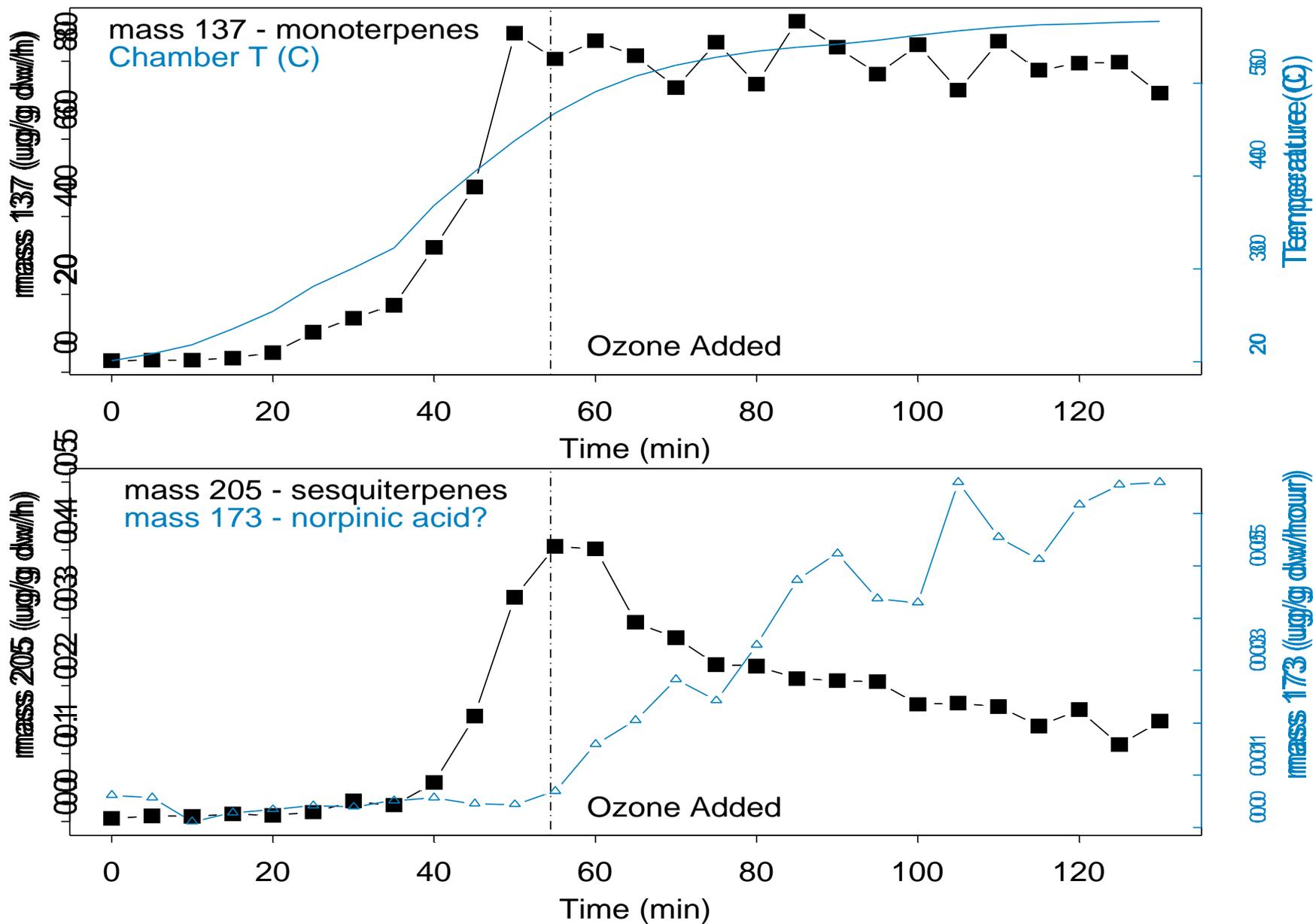
PTR-MS



Chamber Measurements

- Test detection of mono- and sesquiterpenes and their oxidation products
- Compare emissions rates
- Determine temperature response
- Quantify emissions from litter and other plant species
- Preliminary look at ozone oxidation
- Data analysis still in progress!

Ozone Oxidation of Mono- and Sesquiterpenes



Flux Measurements

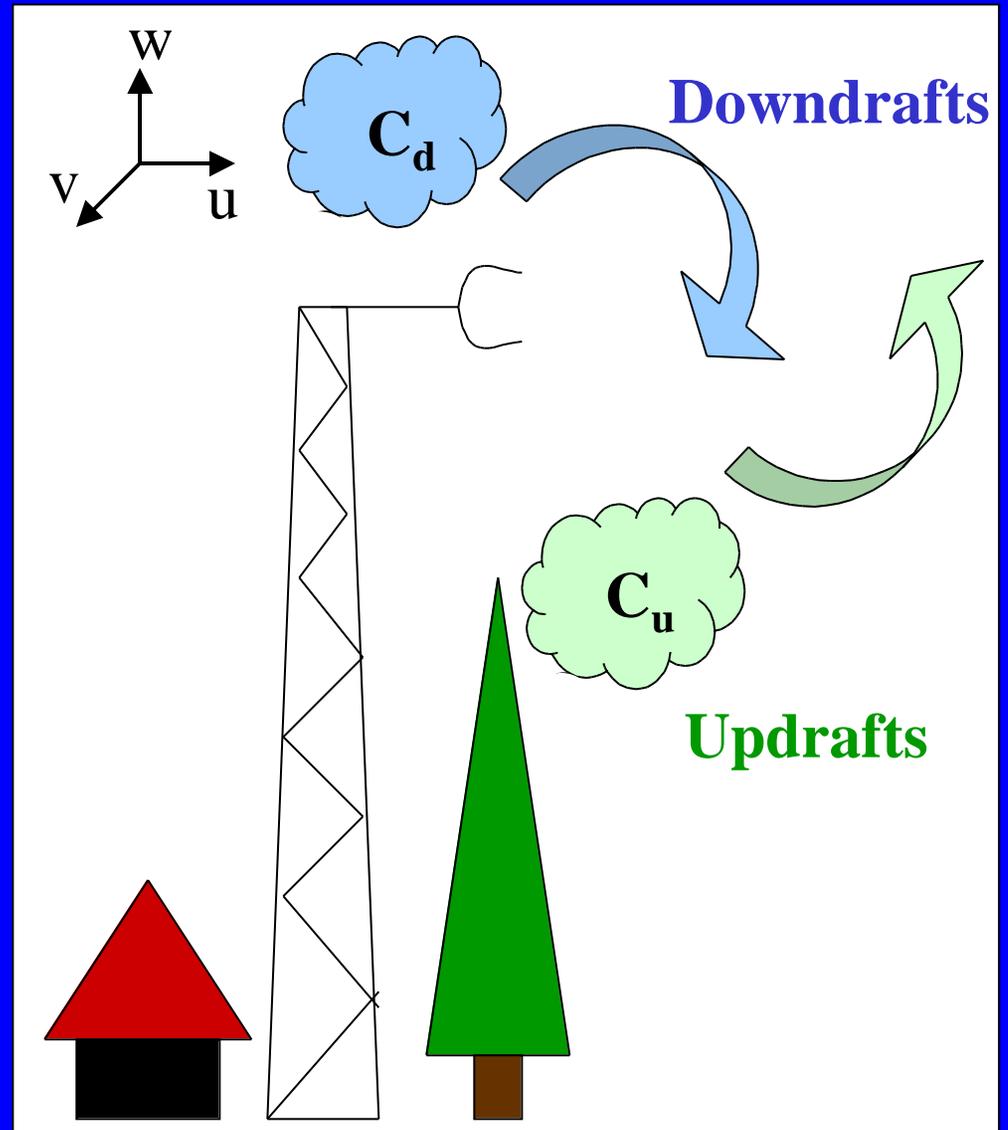
- All monoterpene species share same mass
- PTR-MS Total monoterpenes
- Total vs. speciated monoterpene fluxes
- Total Sesquiterpene Fluxes?
- Terpene Oxidation Products
- Lots of other interesting compounds
- Field deployment last month



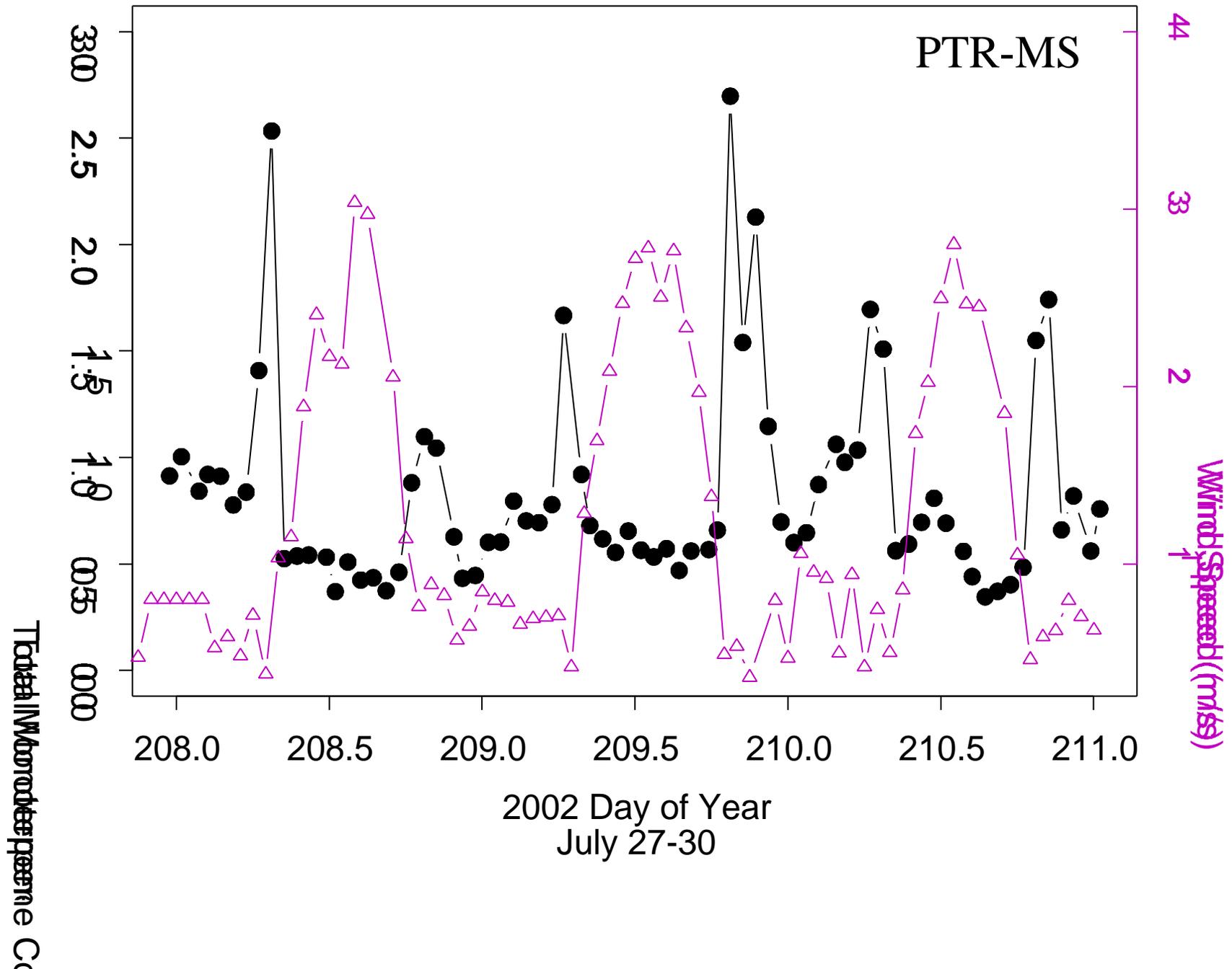


New Measurements

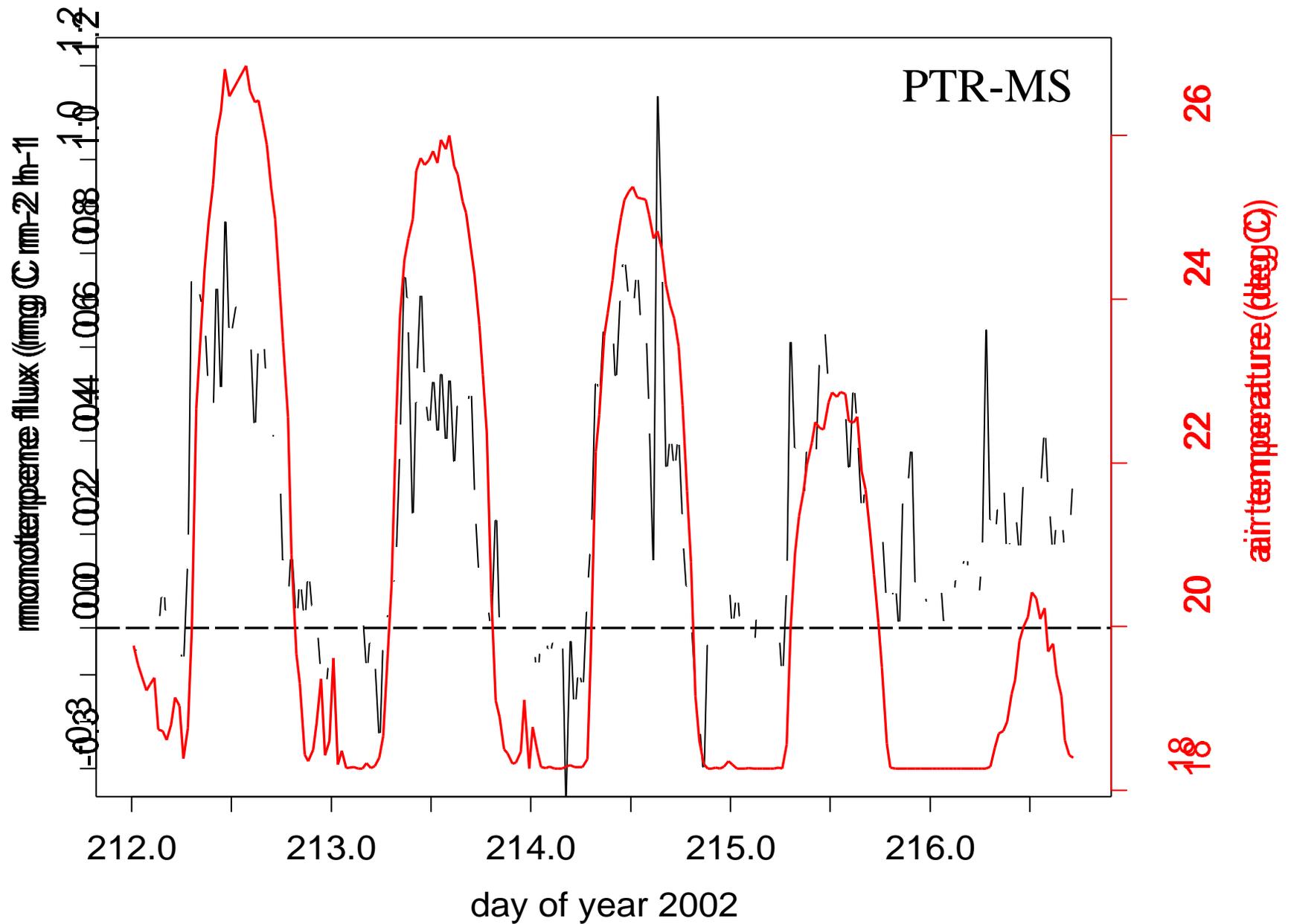
- Flux of **total** monoterpenes and oxidation products
- PTR-MS
- 2 - 8 Hz
- Eddy Covariance
- $F = \overline{w'C'}$



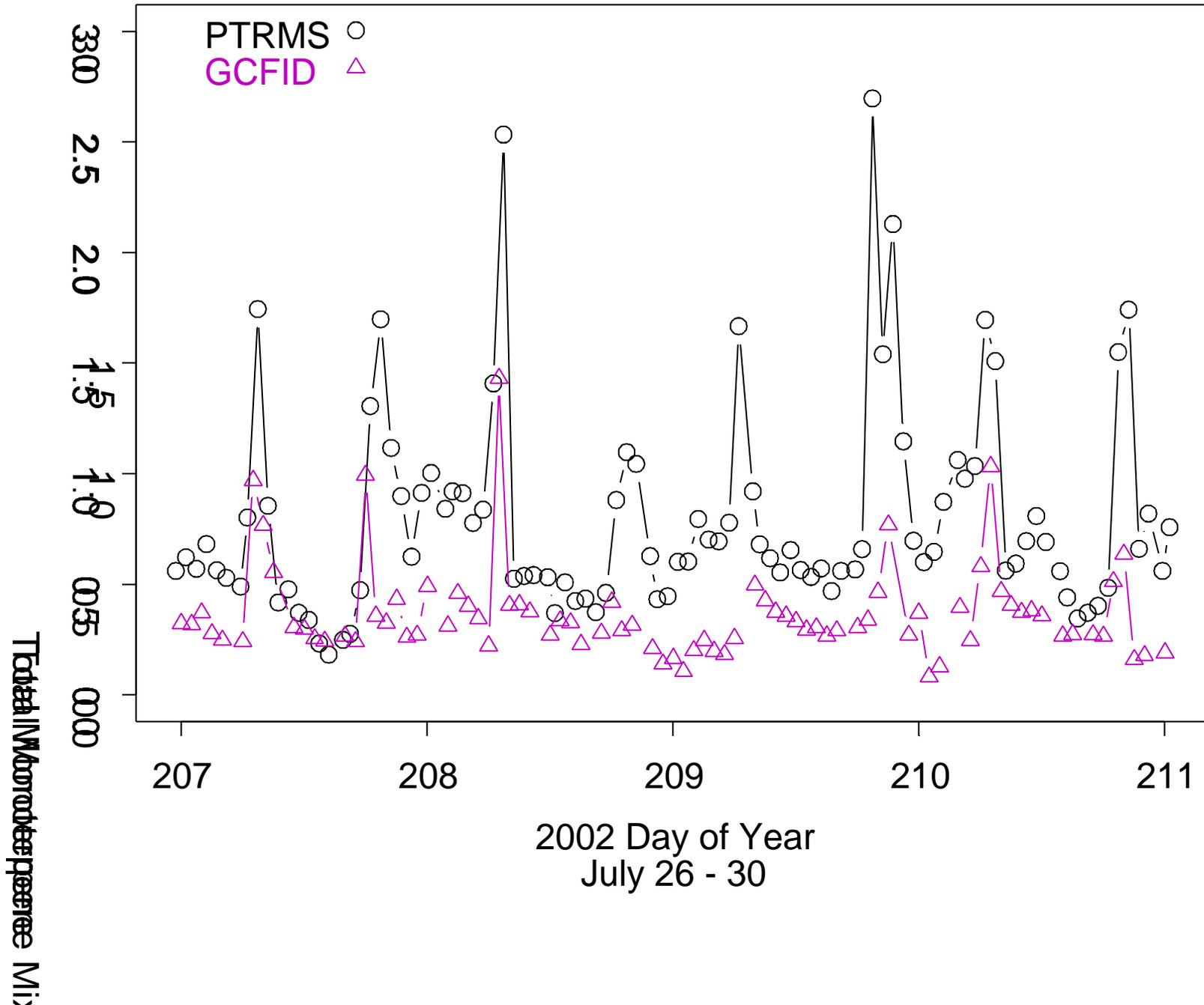
Meteorological Controls on Total Monoterpene Mixing Ratios



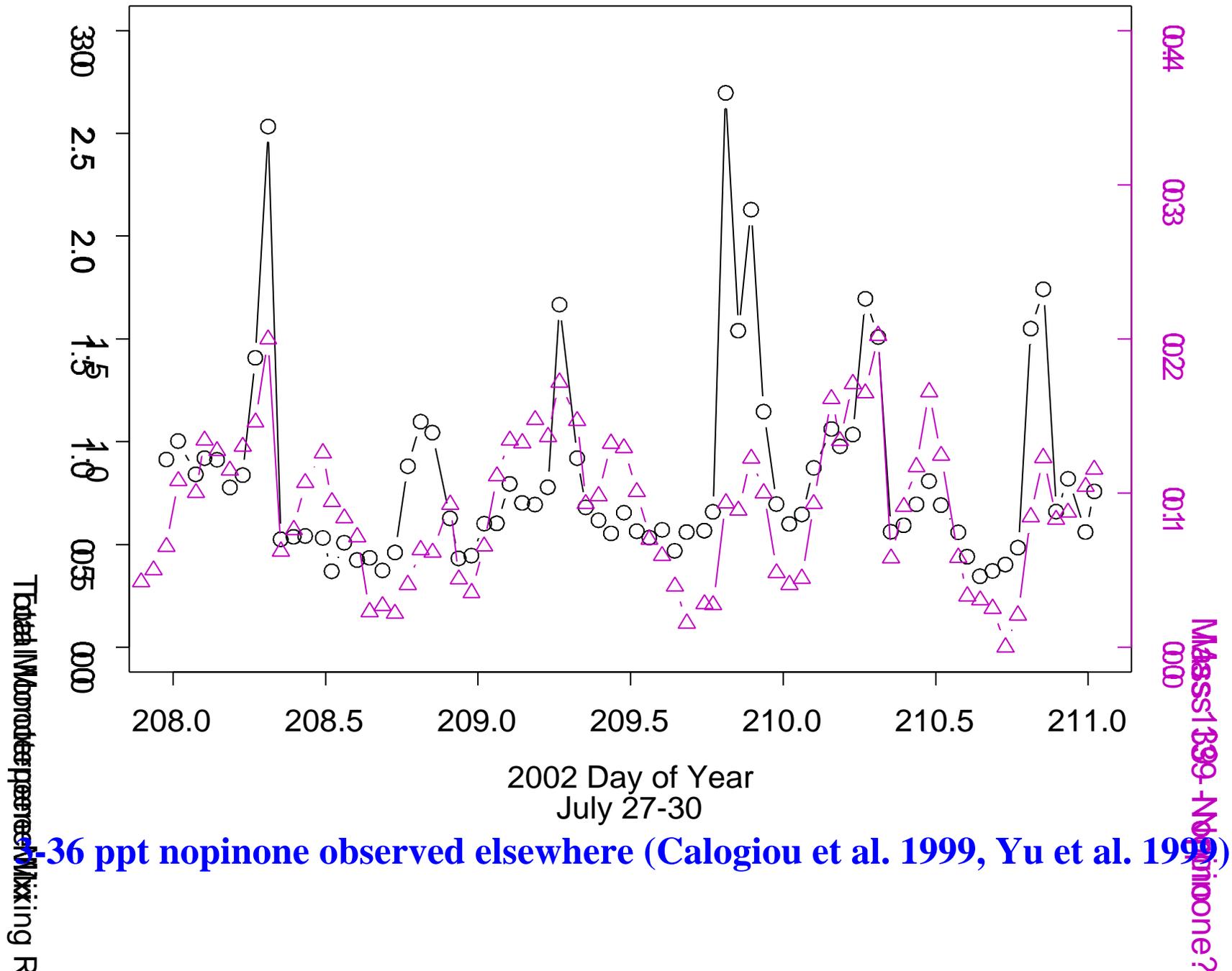
Meteorological Controls on Total Monoterpene Flux



Speciated measurements miss 30 – 50% of total emissions



Observations of Beta-pinene oxidation product?



36 ppt nopinone observed elsewhere (Calogiou et al. 1999, Yu et al. 1999)

Take Home Messages!

- Terpene and oxidation product concentrations and fluxes can be measured by PTRMS-EC
- Terpenes are a natural but poorly characterized source of aerosol
- New Particle Formation Events depend on:
 - local meteorology: temperature, depth of BL
 - concentration of pre-existing aerosol
 - terpene and oxidant species and concentrations
 - Complex system!
- Trees do not cause air pollution!

Thanks to . . .

- DOE – Global Change Education Program
- Blodgett Forest Research Station
- Sierra Pacific Industries
- National Science Foundation
- California Air Resources Board